Accumulation of Sulfur Compounds At the Interface of Paint and Wood Following Exposure to Sulfurous Acid

R. Sam Williams and Thomas A. Kuster
U.S. Department of Agriculture*

John Spence
U.S. Environmental Protection Agency†

Western redcedar *(Thuja plicata)* and southern pine *(Pinus* sp.) strips coated on all surfaces with acrylic latex paint were soaked for 10 days at room temperature in pH 2 sulfurous acid. Matched controls were soaked in distilled water. Analysis of cross sections using energy dispersive X-ray analysis showed an accumulation of sulfur compounds at the paint/wood interface on the specimens treated with acid. The sulfur concentration was highest in the wood just below the primer and decreased at a depth of several wood cells. The effect of the sulfur buildup on paint adhesion was not determined in this preliminary study, but it is the focus of continuing work.

INTRODUCTION

All construction materials eventually degrade when used outdoors. The degradation of many of these materials can be inhibited and/or retarded by maintaining a good coat of paint on them; but, paint also degrades. Degradation of a paint system can occur through one of many mechanisms or a combination of mechanisms. These different mechanisms are manifested as different modes of paint degradation.

Gradual erosion of the paint is the least serious mode of paint degradation and involves only the surface. Erosion is caused mainly by a combination of sunlight, moisture, and oxygen; degradation factors such as wind, particulates, and other chemicals generally are less important. Since erosion affects only the surface of the paint, the paint system can be easily renewed by applying more paint.

Blistering and peeling of paint are more serious degradation modes. The degradation mechanism for these failures is primarily moisture—induced loss of adhesion at the coating/substrate interface. Failure can also occur between paint layers; but in this case, the cause is usually attributed to improper surface preparation prior to painting.[1] Loss of adhesion at the interface is affected by the chemical and physical properties of both the paint and the substrate. This loss of adhesion shortens the service life of the paint system and requires substantially more time and money for refinishing than does erosion.

Blistering and peeling of paint on wood has been the subject of many publications and a few are cited.[2-11] Research on blistering of paint on wood has included effects of paint type and formulation, wood structure, application techniques, weathering, and moisture. The common factor in these studies has been the effect of moisture. Changes in the moisture content of either the paint or wood substrate cause dimensional changes that develop stresses at the interface. These stresses, combined with other physical changes at the interface, such as accumulation of water-soluble extractives, can lead to loss of paint adhesion.

Chemical changes at the interface can also cause loss of adhesion. This is particularly true of wood that has been photochemically degraded prior to finishing. Researchers at the Forest Products Laboratory (FPL) found that when unpainted wood siding was exposed to summer weather conditions, paint adhesion decreased 50% in boards exposed for 16 weeks.[12] In other work at the FPL, it was shown that intermittent soaking of specimens in sulfu-

This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright.

*Forest Service, Forest Products Laboratory, Madison, WI 53705-2398.
†Atmospheric Research and Exposure Laboratory, Research Triangle Park, NC 27711.

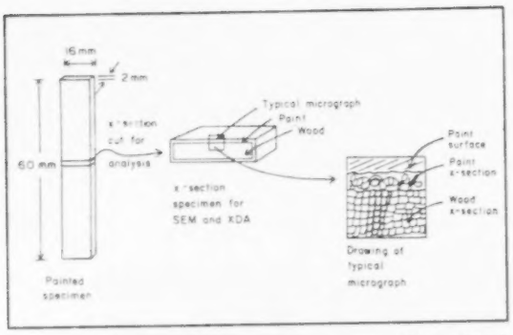

Figure 1—Painted wood strip showing cross section and typical location of SEM and EDXA. (ML875530)

rous,* sulfuric, and nitric acids can accelerate this photochemical degradation.[14] Treatment with sulfurous acid of pH 2 doubled the rate of erosion of western redcedar *(Thuja plicata)* compared with specimens soaked in distilled water.

Although photochemical degradation of wood is not likely if wood is coated with a highly opaque paint, other chemical reactions may occur that weaken wood and thus cause loss of paint adhesion. If acid deposition or its precursors, such as sulfur dioxides, are factors that degrade painted wood, it is necessary that some chemical diffuse through the paint. By limiting the exposure to sulfurous acid, the accumulation of sulfur compounds is a necessary condition for damage to paint systems. In this study, the extent that sulfur dioxide or bisulfite ions accumulated at the paint/wood interface was investigated.

In research using painted wood, the effect of acid conditions on the substrate has not been clearly demonstrated. Ulfvarson and Pattyranie[15] reported that 1% aqueous solutions of HCl and NaOH caused a slight decrease in paint blistering as compared with water. Using buffered solutions at pH 6, 7, and 8, Browne[16] found that free films of oil and alkyd paints swelled differently depending upon the pH and type of paint pigment. Greater swelling occurred at pH 6 and 8, particularly for paint containing zinc oxide. No explanation was given for these results. In other work using free alkyd paint films soaked in sulfurous acid, Svoboda, et al.,[17–19] reported that sulfur dioxide diffused into the paint.

Researchers at the FPL, in cooperation with the U.S. Environmental Protection Agency, are studying the effects of acid deposition on exterior paints. This study is being supported by the National Acid Precipitation Assessment Program (NAPAP) and addresses the effects of both wet (acid rain) and dry deposition on painted wood.

In this preliminary work, painted wood was immersed in sulfurous acid at pH 2 to determine the extent to which sulfur compounds would migrate into the paint/wood system. Further studies are underway to define the chemical reactions that may occur at the paint/wood interface. By linking the chemical changes at the interface with physical changes such as paint adhesion, we hope to determine whether acid deposition affects paint failure such as blistering and peeling.

EXPERIMENTAL

Thin strips of western redcedar *(Thuja plicata)* and southern pine *(Pinus* sp.), 16 × 2 × 60 mm (radial, tangential, longitudinal), were coated with specially formulated low-sulfur paints. The acrylic latex paints had the following compositions:

Primer Composition		Top Coat Composition	
Pigment	20%	Pigment	29%
Titanium dioxide (type IV)[20]	16%	Titanium dioxide (type IV)	14%
Silica	4%	Titanium dioxide (type II)[20]	3%
		Silicates	7%
		Mica	5%
		Tinting colors	trace
Vehicle	80%	Vehicle	71%
Acrylic resin (nonvolatile)	27%	Acrylic resin (nonvolatile)	19%
Additives	3%	Additives	2%
Water	46%	Water	48%
Ethylene glycol	4%	Ethylene glycol	2%

Wood specimens were painted with primer, primer and one top coat, or primer and two top coats. Paint was brush-applied, dried for one day between coats, and cured for one week at laboratory conditions. The specimens were then immersed in pH 2 sulfurous acid at room temperature (22°C) for 10 days in sealed containers. The concentration of the acid was monitored and changed as necessary to maintain constant pH. Following immersion in the acid, the specimens were air dried and cut perpendicular to the grain *(Figure* 1). Cross sections were carbon-coated for scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA).

Micrographs and elemental analysis of cross sections were obtained at several locations for each of the specimens (duplicate specimens of two species with three different paint systems). Analyses were obtained using a JEOL* JSM-840 scanning microscope and a Tracor Northern* TN-5500 energy dispersive spectrometer. Elemental maps of the cross section were collected for Ti, Si, Al, and S for 0.1-sec dwell time at each point of a 128 × 128 grid. Line scans were collected for Ti and S by counting for 30 sec at 100 points in a line across the surface.

RESULTS

Drawings showing the original painted specimen, the cross section, and a typical SEM view are show in *Figure* 1. The micrographs show the cross section of wood and paint with a small portion of the paint surface at the top.

*Although sulfurous acid is either not present or present in minute amounts in aqueous solutions of sulfur dioxide, for simplicity, sulfurous acid is used to designate these solutions.[13]

*The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

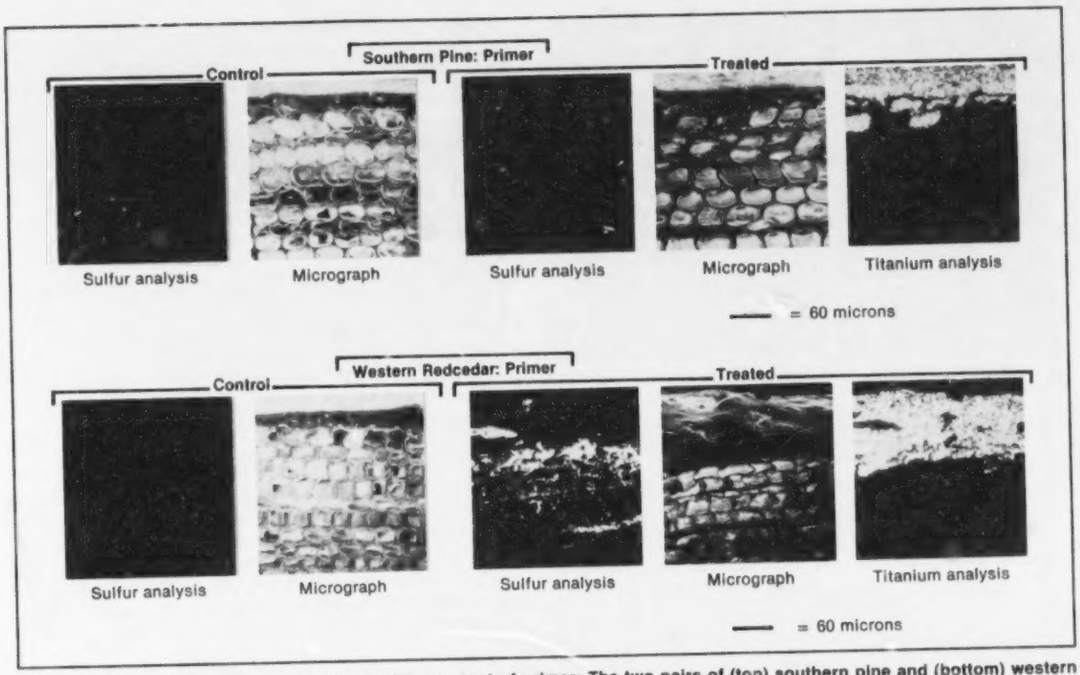

Figure 2—SEM and EDXA of wood painted with one coat of primer: The two pairs of (top) southern pine and (bottom) western redcedar. Photographs on the left are the EDXA sulfur analysis and micrograph for the control soaked in distilled water. The sets of three on the right side are the sulfur analysis, micrograph, and titanium analysis for the specimen soaked in sulfurous acid. (MC879011)

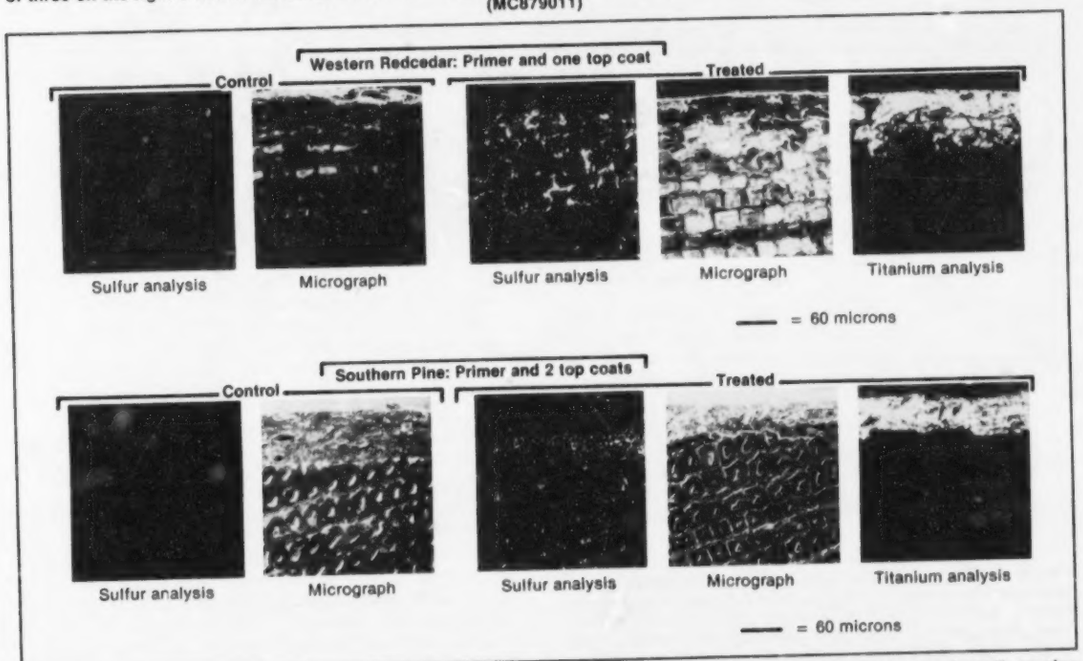

Figure 3—SEM and EDXA of (top) western redcedar painted with one coat of primer and one top coat; and (bottom) southern pine painted with one coat of primer and two top coats. (MC879012)

In *Figure* 2, matched sets of southern pine and western redcedar specimens with one coat of paint are shown. On the left side, the micrograph and the EDXA for the cross section of the controls show no sulfur above background. The right side contains elemental maps of sulfur and titanium of specimen soaked in sulfurous acid.

The map of the titanium helps to define the interface. Titanium dioxide pigment is too large to penetrate the wood cell wall; however, the paint can fill the lumen (cavity of the wood cell), if there is access through cracks or if the cell intersects the surface. The cell wall of the surface cells is easily defined by the areas lacking titanium. The cross sections of wood just below the paint/wood interface clearly show an accumulation of sulfur in the cell wall of the sulfurous acid-treated specimen. The controls show mainly background noise.

Similar results were obtained with all combinations, as shown by western redcedar painted with primer and one top coat and southern pine painted with primer and two top coats (*Figure* 3). A small amount of residual sulfur in the paints was detected above the background noise in a few specimens as shown by the control in *Figure* 3.

Elemental constituents in the cross section of the acid-treated and control specimens were determined. A series of analyses for southern pine painted with primer and two top coats is shown in *Figure* 4 (treated) and *Figure* 5 (control). The sulfur peak is highlighted for the region of interest (2.18 - 2.44 keV). The vertical full scale is the same for all figures.

In *Figure* 6, a line scan of the cross section shows the location of Ti and S with respect to the paint/wood interface. The Ti defines the limits of paint penetration into the wood. The S trace shows an increase in sulfur at the interface and substantial penetration (approximately 200 μm) of sulfur compounds into the wood. With about the same vertical full scale as in *Figure* 6, the control (*Figure* 7) shows no sulfur in the primer or the wood.

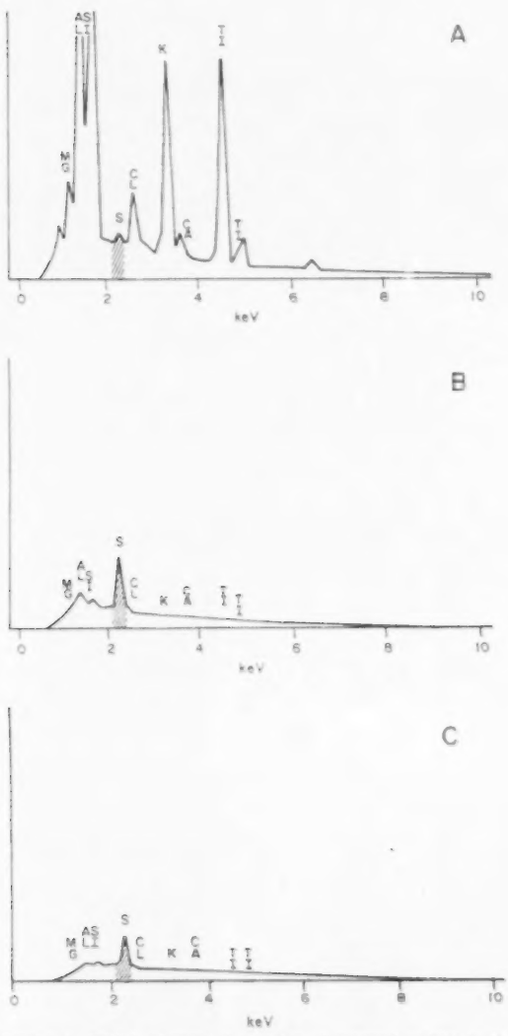

Figure 4—EDXA elemental spectra at several points in the cross section of western redcedar with one coat of primer and two top coats and soaked in sulfurous acid. The sulfur peak is highlighted. Vertical full scale = 4,096 counts. Analysis at (A) middle of the paint cross section; (B) wood cell wall at the wood surface; and (C) eighth wood cell below the paint/wood interface. (ML875527, ML875528)

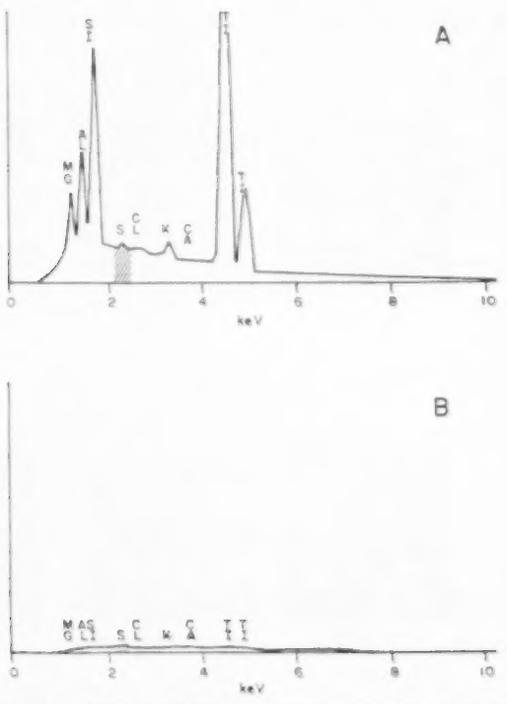

Figure 5—Same paint system (*Figure* 4) soaked in distilled water. Analysis at (A) middle of the paint cross section; and (B) wood cell at the wood surface. (ML875529)

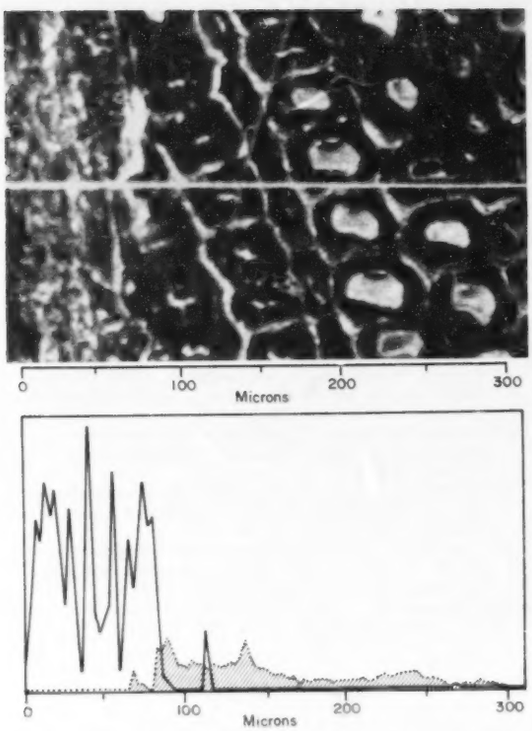

Figure 6—SEM and line scan of sulfurous acid treated southern pine painted with one coat of primer and two top coats. Vertical full scale = 10,643 counts. —— Tl, - - - S. (ML875532)

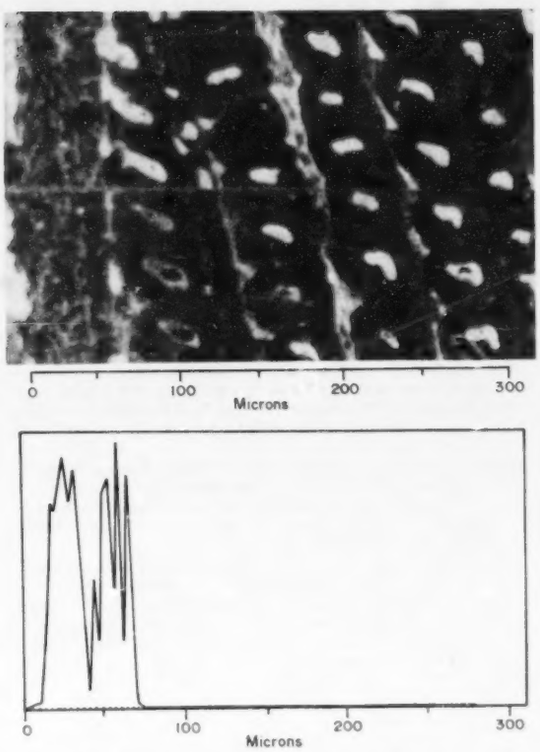

Figure 7—SEM and line scan of untreated southern pine painted with one coat of primer and two top coats. (ML875531)

DISCUSSION

The small amount of sulfur in the paint film compared to that in the wood was somewhat surprising in light of the previous work by Svoboda, et al.,[17] that showed sulfur compounds present in alkyd paint films. The difference in the amount of sulfur compounds in the two materials may be caused by differences in reactivity with sulfurous acid (i.e., latex paint films examined in this study may have been more resistant to sulfurous acid). Unreacted sulfurous acid in the paint film probably evaporated prior to analysis. Since the sulfur is found almost exclusively in the wood, the sulfur dioxide or bisulfite ions appear to have diffused through the paint film and may have reacted with lignin in the wood to form lignosulfonic acid. In acid sulfite pulping of wood, bisulfite ions react with the benzylic carbon atoms in phenolic and nonphenolic moieties in the lignin to form lignosulfonic acid.[21] In addition, lignosulfonic acids are stronger than sulfurous acid and would probably hydrolyze some of the hemicelluloses and cellulose. The result of these reactions could change the surface characteristics of the wood and possibly degrade the wood at the interface. It is not possible to prove actual wood degradation by EDXA; however, further work is planned to measure the change in adhesive strength and to establish if chemical changes occur at the paint/wood interface.

CONCLUSIONS

Sulfur compounds, either as bisulfite ions or sulfur dioxide dissolved in water, migrated through an acrylic latex paint system and accumulated at the wood/paint interface. High sulfur concentrations were found from the interface to 200 μm into the wood. This was observed for western redcedar and southern pine painted with primer, primer and one top coat, or primer and two top coats. In this work, it was not possible to identify the sulfur compounds in the wood.

ACKNOWLEDGMENTS

The authors thank Emil Iraola, Olympic Home Care Products Co., for formulating and supplying the paint. This work was partially supported by IAG No. DW 129 31510-01-3 with the U.S. Environmental Protection Agency.

References

(1) U.S. Department of Agriculture, "Intercoat Peeling of House Paints," Research Note FPL-0127, U. S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, 1966.

(2) Browne, F.L., "Understanding the Mechanisms of Deterioration of House Paint," *Forest Prod. J.*, *9* (11), 417-427 (1959).

(3) Brunt, N.A., "Blistering of Paint Layers as an Effect of Swelling by Water." *J. Oil & Colour Chemists' Assoc.*, *47*(1), 31-42 (1964).

(4) Harris, J., "A Study of House Paint Properties," Research Paper No. 180, National Research Council, Division of Building Research, Ottawa, Canada, 1963. Reprinted from *Can. Paint & Varnish Mag.*, *37* (2), 22 and *37* (3), 42 (1963).

(5) Holbrow, G.L., "Blistering of Paints on Wood," *Review of Current Literature on Paint and Allied Industries*, *37*(265), *409*(7) (1964).

(6) Hopkins, C.Y. and Smart, B.C., "Experimental Study of Blistering of Paints on Wood," *Chemistry in Canada* (9), 35 (1953).

(7) Johnson, J.A., "Correlation Between Paint Permeability and Blistering of Paint on Wood," *Official* DIGEST, *37*, No. 490, 1436 (1965).

(8) Ulfvarson, U. and Pattyranie, C., "The Blistering of Paints on Wood Induced by Moisture. I. The Influence of Some Structural Variables of Pinewood on Blistering Induced by Moisture of an Alkyd Paint System," *J. Oil & Colour Chemists' Assoc.*, *55*, 207-218 (1972).

(9) U.S. Department of Agriculture, "Blistering, Peeling, and Cracking of House Paints from Moisture," Research Note FPL-0125, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, 1970.

(10) Veer, J.J.G., "Moisture Blistering of Paints on Wood," *Forest Prod. J.*, *7*, 342-344 (1957).

(11) Veer, J.J.G. and King, F.W., "Moisture Blistering of Paints on House Siding," Publication No. 1024, Department of Forestry, Ottawa, Canada, 1963.

(12) Williams, R.S., Feist, W.C., and Winandy, J.E., "Paint Adhesion to Weathered Wood," JOURNAL OF COATINGS TECHNOLOGY, *59*, No. 749, 43 (1987).

(13) Cotton, F.A. and Wilkinson, G., "Advanced Inorganic Chemistry, a Comprehensive Text," Interscience Publishers, p 423-425, New York, NY, 1962.

(14) Williams, R.S., "Effects of Dilute Acid on the Accelerated Weathering of Wood," *J. Air Pollution Control Assoc.*, *38*(2), 148-151 (1988).

(15) Ulfvarson, U. and Pattyranie, C., "The Blistering of Paints on Wood Induced by Moisture. II. The Influence of Various Treatments of Pinewood on Blistering Induced by Moisture," *J. Oil & Colour Chemists' Assoc.*, *55*, 219-226 (1972).

(16) Brown, F.L., "The Absorption of Water, Swelling, and Solubility of Free Films of Paint," Reprint 252, Forest Products Research Society, Madison, WI, 1953.

(17) Svoboda, M., Klicova, H., and Knapek, B., "The Penetration of Sulphur Dioxide into Alkyd Resin Films," *J. Oil & Colour Chemists' Assoc.*, *52*, 677-686 (1969).

(18) Svoboda, M., Klicova, H. and Knapek, B., "Penetration of Sulfur Dioxide into an Alkyd Paint Film," *Zashchita Metallov*, *6*(6), 644-647 (1970).

(19) Svoboda, M., Klicova, H. and Knapek, B., "Possible Reduction of the Penetration Rate of Sulfur Dioxide into a Paint Film," *Zashchita Metallov*, *9*(3), 301-303 (1973).

(20) "Designation: D 476-73 (Reapproved 1979) Standard Specification for Titanium Dioxide Pigments," Annual Book of ASTM Standards, Vol. 06.02, Philadelphia, PA, 1983.

(21) Gellerstedt, G., "The Reactions of Lignin During Sulfite Pulping," *Svensk Papperstid.*, No. 16, 537-543 (1976).

☆U. S. GOVERNMENT PRINTING OFFICE: 1989/643-043/00002